State of California

M E M O R A N D U M

To : Ron Oshima, Chief
Environmental Monitoring &
Pest Management Branch
1220 N Street
Sacramento, CA 95814

Date : August 18, 1989

Subject : Application Site Monitoring Data for Methyl Parathion

Robert Barham, Chief
Toxic Air Contaminant
Identification Branch
From : Air Resources Board

Attached is our report on application-site monitoring for methyl parathion. The monitoring was conducted in May 1989 in Sutter County. This monitoring was conducted to fulfill your request of April 22, 1988, to provide supplementary exposure data.

If you have questions regarding this report, please call me at 322-7072 or have your staff contact Lynn Baker at 445-6532.

cc: Al Perrin, Jr., Sutter County APCO
Dr. Michael Lipsett, DHS

Attachment

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING REPORT

Methyl Parathion Monitoring in Sutter County

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C89-024

Report Date:

APPROVED:

_____, Project Engineer
Testing Section

Peter K. Ouchida, Manager
Testing Section

_____, Chief
Engineering Evaluation Branch

Methyl Parathion Monitoring in Sutter County

This report presents the results of field application monitoring of methyl parathion in Sutter County. The results are based on samples collected and analyzed by the Air Resources Board (ARB) staff using ARB developed sampling/analysis methods. The results have been reviewed by the staff and are believed to be accurate within the limits of the methods. However, data may have been affected by variables which were not apparent during the monitoring, such as proximity of samplers to the plume after application of the pesticide.

Acknowledgments

The project engineer was Don Fitzell. The Instrument Technician was Jack Rogers of the ARB. Assistance was provided by Lynn Baker and Jay Emerson of the ARB's Toxic Air Contaminant Identification Branch. Chemical analyses were performed by Mike Poore, of the ARB's Northern Laboratory Branch. The ARB staff is also grateful of the assistance provided by Steve Protine of the Sutter County Agricultural Commissioner's Office, VA Farms and Bill Porter of Farm Air Flying Services, Inc., in coordinating the field application of methyl parathion.

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Methyl Parathion Monitoring in Sutter County

I. INTRODUCTION

At the request of the California Department of Food and Agriculture (CDFA) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted source impacted ambient monitoring for methyl parathion in Sutter County during the month of May 1989.

A set of ambient samplers were stragically placed upwind and downwind of a flooded rice field to monitor ambient levels of methyl parathion before, during and after its application to the field. This study was a coordinated effort between ARB staff and personnel from CDFA. The ARB's monitoring program was conducted in response to Section 14022(c) of the Food and Agricultural Code, which requires the ARB to document the level of airborne emissions of pesticides when requested by CDFA.

II. PESTICIDE DESCRIPTION

Methyl parathion is an organophosphate insecticide widely used in agriculture because of its high pesticidal activity and relatively low persistence in the environment. It is used on a large variety of crops with application levels ranging from 1/4 to 2 lbs./acre depending upon the type of crop.

Methyl parathion is toxic if swallowed, inhaled, or adsorbed through the skin. Because of its toxicity, it is a restricted material and may only be applied under permit and use conditions administered by the local county agricultural commissioner. Regulatory procedures require users to file pesticide use reports with the county whenever methyl parathion is applied. This information, along with the pesticide use reports filed in other counties, provides the basis of the annual statewide Pesticide Use Report (PUR).

III. SAMPLING LOCATIONS

Based on site specific parameters supplied by the ARB the sampling site was chosen by Steve Protine of the Sutter County Agricultural Commissioner's Office. Factors considered were; location, accessibility, isolation from other fields being sprayed at the same time and cooperation of the grower.

IV. SAMPLING METHODOLOGY

The sampling method used during this study (see Appendix A) required passing measured quantities of ambient air through XAD-2 resin tubes. Any methyl parathion present in the sampled ambient air is captured by the XAD adsorbent contained in the tubes. Subsequent to sampling, the resin tubes were transported in an iced container to the ARB's Northern Laboratory Branch in Sacramento for sample recovery and analysis (See Appendix B.)

Sampling trains designed to operate for 72 hours after application were set up at the three sampling sites identified in Figure 1 of this report. The sampling sites were designed to be (approximately); 15 yards upwind, 15 yards downwind and 150 yards downwind of the field. Duplicate (co-located) samples were taken at each sampling site. An on-site meteorological station measured wind direction and speed to determine upwind/downwind sampling locations with respect to the field.

Sampling was planned for a 72 hour period that included; one background sample taken before pesticide application, one sample taken during pesticide application and six samples taken after the application (see attached protocol, Appendix A, for sampling schedule.)

Each sample train consisted of: a portable sampling box, teflon tubing, stainless steel fittings, train support, 12 VDC battery and two XAD-2 tubes each with its own pump and rotometer. A diagram of the sampling train is shown in Figure 2. Each resin tube was prepared for use by breaking off each sealed glass end and then immediately inserting the tube into a Teflon fitting. The resin tube was oriented in the sampling train according to a small arrow printed on the side of each tube indicating the direction of flow. Covers were wrapped around the tube to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow adjusted with a flow meter and metering valve to an indicated reading of 1.5 liters per minute (lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free if the indicated flow dropped to zero. Upon completion of a successful leak check, the flow rate was rechecked and recorded along with date, time, and site location.

At the end of each sampling period the final indicated flow rate and the "stop" date and time were recorded. The two XAD-2 resin tubes were then removed from the sample train, end caps installed on both ends, and identification labels affixed to each resin tube. Each tube was then placed in a culture tube with a screw cap and stored with ice in a covered chest until the tubes were delivered to the ARB's Northern Laboratory Branch for analysis.

All rotometers were calibrated with a bubble meter prior to use in the field and rechecked after the test.

V. ANALYTICAL METHODOLOGY

All samples were analyzed by the ARB's Northern Laboratory Branch, using Method ADDL003, Method for the Determination of Selected Organophosphate Pesticides in Ambient Air (see Appendix C.) When the exposed XAD-2 sorbant tubes arrived at the laboratory, they were frozen until desorbed with 2 ml of isooctane/acetone (80/20 v/v). An aliquot of that solution was injected into a gas chromatograph with a 30m x 0.32mm i.d. DB-5 fused silica capillary column and a thermionic specific detector.

VI. RESULTS

The results of this test are shown in Table 1, SAMPLE CONCENTRATIONS, Table 2, METEOROLOGICAL DATA and Table 3, NORTHERN LABORATORY BRANCH QUALITY ASSURANCE DATA. The data for Table 2 was obtained from the ARB Pleasant Grove Station and an on site meteorological station. The meteorological data for the first twenty-four hours is based on the on-site station; latter data is from the Pleasant Grove Station. Wind speed determined by the Pleasant Grove Station has been converted from knots to miles per hour.

As indicated in SAMPLING METHODOLOGY, the samplers were designed to be upwind, downwind and approximately 150 yards downwind from the field. Prior to the application the wind was light and variable; therefore the samplers were set up based on prevailing wind patterns (north to south). This resulted in the second downwind sampler (designated S-2) to be placed approximately 250 yards south of the field; this being the closest practical spot to the desired 150 yards downwind. During the application and for several hours afterward (through samples 4N and 4S) the wind remained light and variable; this makes differentiating upwind from downwind impossible. Before collecting samples 5, 6 and 7 the wind shifted and came strongly out of the south. This resulted in samples 5N, 6N and 7N actually being the downwind samples for these periods. Because of another wind shift sample 8S was then the downwind sample.

The background samples (1N, 1S and 1S-2) all were below the detection limit as expected. Significant levels were found during the application and for fifteen hours afterward. After fifteen hours all results were below the five ppt level, if detected at all.

TABLE 1 SAMPLE CONCENTRATIONS

	Replicate Samples		Wind	
SAMPLE ID#	#1 (ppt)[1]	#2 (ppt)[1]	direction[2]	speed (mph)
1N	<15.8	<15.8		
1S (background)	<16.0	<16.0	SE	02
1S-2	<20.9	<20.9		
2N	50.9	44.5		
2S (appl. +1 hr)	21.3	14.2	SW	04
2S-2	<16.5	<16.5		
3N	12.0	18.0		
3S (1-3 hr)	18.5	18.5	W	04
4N	9.6	12.9		
4S (3-7 hr)	29.0	22.6	W	04
5N	30.4	27.9		
5S (7-15 hr)	8.4	10.1	S	08
6N	6.5	6.5		
6S (15-24 hr)	<3.2	<3.2	S	15
7N	4.8	3.2		
7S (24-48 hr)	0.8	<0.8	S	14
8N	2.3[3]	2.8[3]		
8S (48-72 hr)	3.2	2.3	N	07

N = north of the field about 20 yards.
S = south of the field about 20 yards.
S-2 = south of the field about 250 yards.
< = indicates that the level was below detectable limits. Values vary because of differences in the volume sampled.

(1) ppt = parts per trillion (v/v)

(2) direction = wind is coming from

(3) These values are minimums because the pump battery had run down and total volume sampled was less.

TABLE 2 METEOROLOGICAL DATA

Format: XX YY
XX = wind direction
YY = wind speed (mph)

Hour (PDT)	May 16	May 17	May 18	May 19
0100	--	S 07	SE 14	N 02
0200	--	S 09	S 14	NW 08
0300	--	S 12 (5)	SE 10	NW 07
0400	--	S 07	SE 10	N 06
0500	--	S 08	SE 12	NW 06
0600	--	S 09	SE 12	NW 06
0700	--	S 12	SE 10 (7)	N 05 (8)
0800	SE 02 (1)	S 15	SE 12	N 09
0900	S 02	S 15	S 08	N 10
1000	--	S 15 (6)	SW 07	N 08
1100	--	SW 16	NW 05	N 08
1200	--	SW 15	NW 08	N 05
1300	SW 04 (2)	SW 15	NW 07	N 05
1400	SW 03	SW 16	NW 10	--
1500	W 04 (3)	SW 17	NW 08	--
1600	W 03	SW 21	NW 08	--
1700	W 02	SW 24	NW 07	--
1800	W 03 (4)	SW 23	N 07	--
1900	S 05	SW 23 (7)	N 07 (8)	--
2000	S 05	S 21	NE 08	--
2100	S 06	S 17	N 07	--
2200	S 07 (5)	S 18	NW 06	--
2300	S 06	S 15	NW 03	--
2400	SE 07	SE 15	N 03	--

( ) indicates sample number being taken during that interval.

Source: Air Resources Board Pleasant Grove Station - 1989 and on site meteorological station.

TABLE 3 NORTHERN LABORATORY BRANCH QUALITY ASSURANCE DATA

Results of Methyl Parathion Spiking

SAMPLE	UG/SAMPLE	SAMPLE	UG/SAMPLE
SA #1 *	1.66	SA #2 *	1.46
SB #1 **	0.22	SB #2 **	0.24

* NLB spiked sample: Nominal amount = 1.50 ug/sample
** NLB spiked sample: Nominal amount = 0.20 ug/sample

Recovery and Storage Data for Methyl Parathion

CONCENTRATION, UG	RECOVERY, UG (1)	RECOVERY AFTER 14 DAYS, UG
0.20	0.22 ± 0.031	0.20 ± 0.028
0.60	0.57 ± 0.047	0.61 ± 0.066
1.00	1.03 ± 0.088	0.97 ± 0.106

(1) All recoveries are calculated from duplicate analyses of three spiked tubes at each concentration.

Sampling Efficiency and Conversion Study for Methyl Parathion

CONCENTRATION, UG	RECOVERY, UG (2)
0.20	0.18 ± 0.028
1.00	1.05 ± 0.120

(2) All recoveries are based on duplicate analyses of three spiked tubes at each concentration. One tube per each concentration was sampled at the NLB laboratory site for 24 hrs at a flow rate of 2 liters/min, then analyzed.

TABLE 4 SAMPLE DATA

Sample	Duplicates ug/Sample	*	Sampling time (hr.)	Sampling volume (liter)
1N	<.02	<.02	1.23	110.7
1S	<.02	<.02	1.22	109.8
1S-2	<.02	<.02	.93	83.7
2N	.08	.07	1.53	137.7
2S	.03	.02	1.37	123.3
2S-2	<.02	<.02	1.18	106.2
3N	.02	.03	1.62	145.8
3S	.03	.03	1.58	142.2
4N	.03	.04	3.03	272.7
4S	.09	.07	3.02	271.8
5N	.36	.33	11.53	1037.7
5S	.10	.12	11.55	1039.5
6N	.04	.04	5.98	538.2
6S	<.02	<.02	6.00	540.0
7N	.12	.08	24.33	2189.7
7S	.02	<.02	24.28	2185.2
8N	.05	.06	21.05	1894.5
8S	.07	.05	21.52	1936.8

* to convert to volume:

$$V = \frac{nRT}{P} = \frac{\left(\frac{\quad g \quad}{(279.2025\ g/m)}\right)(8.21 \times 10^{-2}\ l\text{-atm/m-}^{o}K)(298^{o}K)}{1\ atm}$$

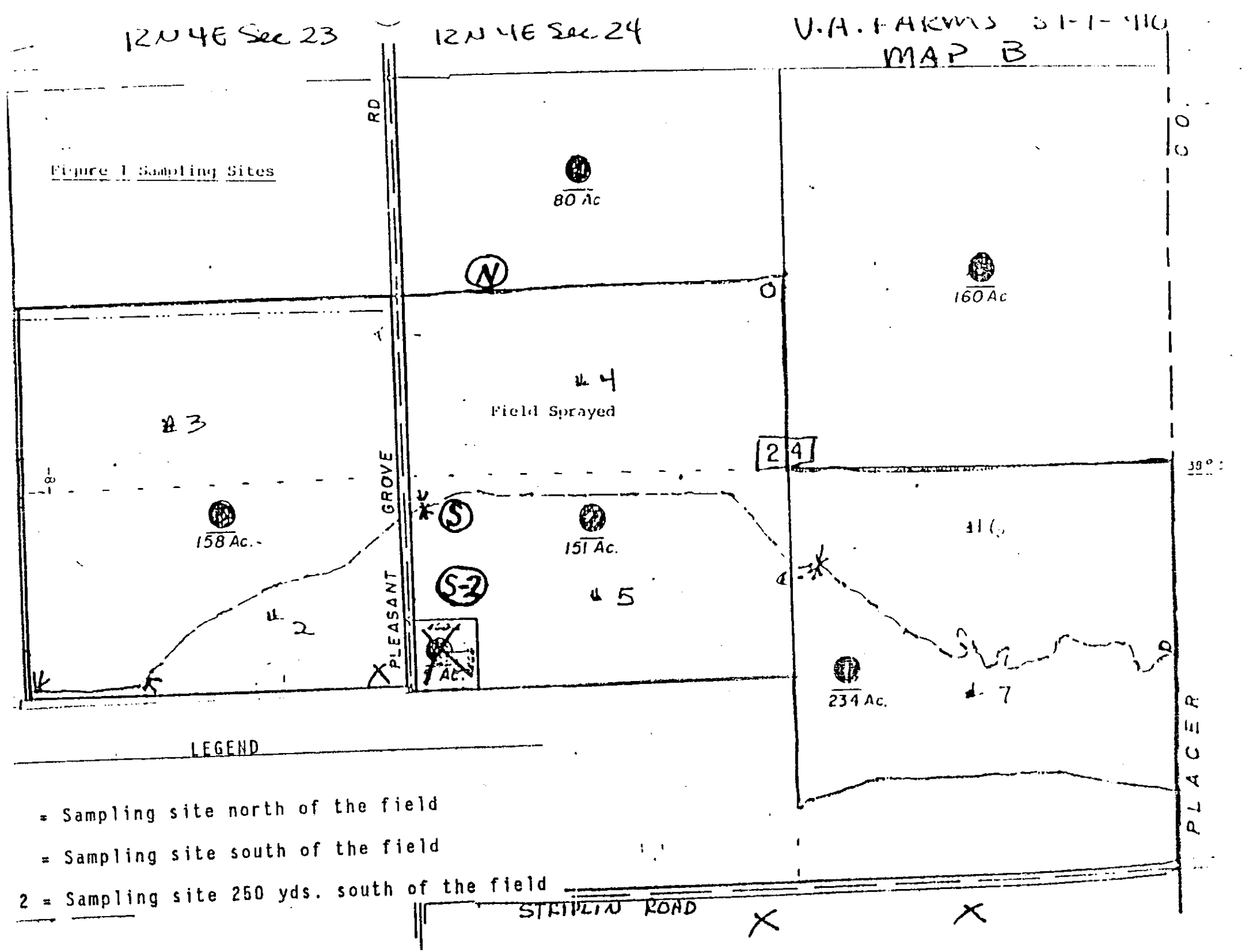
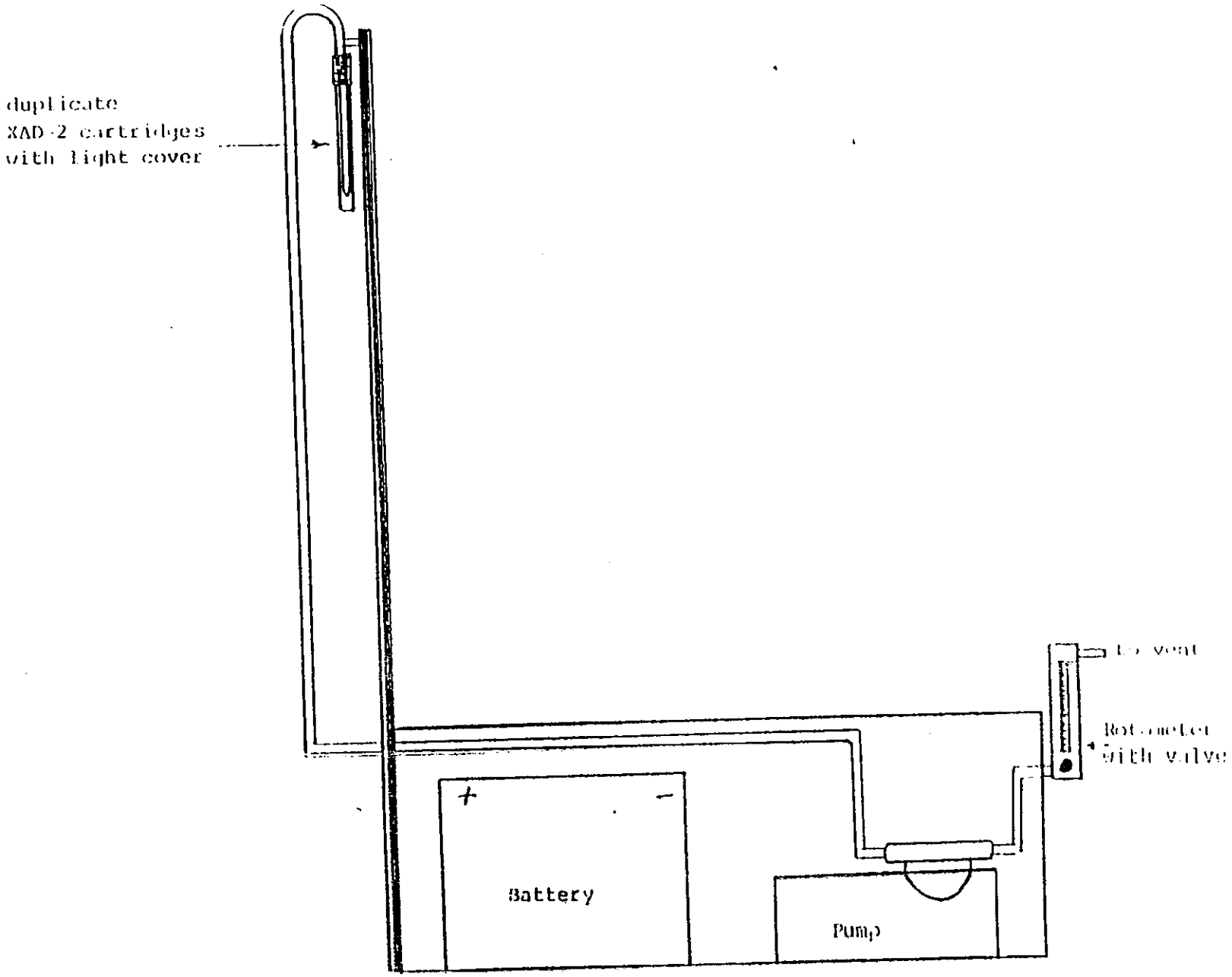

12N 4E Sec 23
12N 4E Sec 24
V.A. FARMS 3-1-'10
MAP B
Figure 1 Sampling Sites
RD
80 Ac
160 Ac
N
#4
Field Sprayed
#3
24
GROVE
158 Ac.
S
151 Ac.
S-2
#5
#2
PLEASANT
AC.
#1
234 Ac.
#7
CO.
PLACER
LEGEND
= Sampling site north of the field
= Sampling site south of the field
2 = Sampling site 250 yds. south of the field
STERLING ROAD

Figure 2 Pesticide Sampling Apparatus



Appendix A

Sampling Protocol

Appendix A

State of California

M E M O R A N D U M

To : James Behrmann, Manager
Toxics Program Support Section

Date : April 12, 1989

Subject : Methyl Parathion
Sampling Plan

Peter Ouchida, Manager
Testing Section
From : Air Resources Board

Don Fitzell of my staff will be sampling for methyl parathion at a field application in May 1989. (A specific date and field to be sampled has yet to be determined.) Collocated samplers will be stationed about 15 meters upwind and downwind of the application field and, if reasonable, 150 or greater meters downwind of the application field. They will also be located in accordance with US EPA ambient monitoring criteria (see Table 1 attached). After the application, the stations will not be moved even if there is a wind change.

Samples will be collected at the maximum flow ratte of the battery powered pumps up to a maximum flow of 2 liters per minute (lpm). (A procedure for sampling at 20 lpm or greater will not be developed by May.) The samples will be collected by passing ambient air through XAD-2 sampling tubes with the same lot numbers. During sampling each resin tube will be protected by a light shield and rain shield. Triplicate samples will be taken at each site. After sampling, the resin tube will be capped, placed in a culture tube with a screw cap and stored with ice in a covered ice chest. When all of the samples are collected, duplicates from each site will be sent to ARB's Northern Laboratory Branch in Sacramento and the remaining replicate from each site will be transported to the ARB Southern Laboratory Branch in El Monte for recovery and analysis.

The sampling schedule for all stations is as follows:

	Site		
	up-wind	down-wind	150 yds down-wind
- Background sample (1 hr. sample prior to application).	3	3	3
- Application + 1 hr. after application combined sample.	3	3	3
- 2 hr. sample from 1 to 3 hours after the application.	3	3	-
- 4 hr. sample from 3 to 7 hours after the application.	3	3	-
- 8 + hr. sample from 7 to 15 hours after the application.	3	3	-
- 9 + hr. sample from 15 to 24 hours after the application.	3	3	-
- 1st 24 hour sample starting at the end of the 9 hr. sample.	3	3	-
- 2nd 24 hour sample starting 24 hrs after the end of the 9 hr. sample.	3	3	-

Since methyl parathion is highly toxic (see attached memo from Dept. of Food and Agriculture concerning 24 hour and 14 day reentry restrictions) and the sampling crew is not trained nor paid to work in hazardous areas, the application samples will be collected when the sampling team feels it is safe to enter the area. The 8 hr. and/or 9 hr. samples may be extended or combined at the discretion of the sampling team in order to establish a convenient time for changing sample tubes. During the shorter sampling periods, when the test crew is onsite, a portable weather station will record wind direction, wind run over time, and temperature. The ARB is connected by telemetry to many weather stations at airports throughout the state. This telemetry system can be used to provide supplemental wind data as needed.

For quality assurance, the sampling team will create field blanks at the rate of 1 per station per day of sampling. At the discretion of the laboratory, spiked samples may be sent into the field with the sampling team. The laboratory will determine spike recoveries (3 replicates of 3 concentrations), conversion/collection efficiency (3 replicates of 2 concentrations), and storage stability (3 replicates of 2 concentrations at $0^{o}C$).

All sqamples will be analyzed according to the method outlined in ADD L003. In addition, the breakdown compound, methyl paraoxon will be analyzed for unless unforeseen complications occur.

If there are any comments or questions, contact Don Fitzell (445-0618) or David Todd (323-2407) of my staff.

Attachments

cc: Lynn Baker
Don Fitzell
David Todd
Jim Shikiya
Henry Mano

TABLE 1

Pesticide Monitor Siting Criteria Summary

The following probe siting criteria apply to pesticide monitoring and are summarized from the EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart.

Appendix B

Northern Laboratory Branch Results

Appendix B

State of California

M E M O R A N D U M

To : George Lew, Chief
Engineering Evaluation Branch
Monitoring and Lab. Division

Date :May 25, 1989

Subject : Methyl Parathion
Study Results

/s/
Through: Don Crowe, Chief
Northern Laboratory Branch

/s/
From : Michael Poore, Laboratory Services Section, NLB

This memo contains the report of the methyl parathion analyses of the XAD-2 resin samples received from Don Fitzell on 5/16/89 and 5/19/89. The data from those analyses are compiled in Table 1. The data is reported as "Total ug/sample" in that sample locations and volumes were not supplied to the laboratory. Two samples for each sample identification were supplied. These are reported as #1 and #2; the designations are assigned by the laboratory for clarity purposes only. The two samples were not individually identified by the sampling personnel.

Table 2 contains the required recovery and storage data for methyl parathion. Table 3 contains the collection/conversion data. The methyl paraoxon standard ordered for this study was backlogged and has not yet been received. When the standard is available, the chromatographic traces will be examined for the presence of methyl paraoxon, and an additional report will be issued.

TABLE 1
RESULTS OF METHYL PARATHION MONITORING PROGRAM

SAMPLE	UG/SAMPLE	SAMPLE	UG/SAMPLE
1N #1	<0.02	1N #2	<0.02
1S #1	<0.02	1S #2	<0.02
1SA #1	<0.02	1SA #2	<0.02
2N #1	0.08	2N #2	0.07
2S #1	0.03	2S #2	0.02
2SA #1	<0.02	2SA #2	<0.02
3N #1	0.02	3N #2	0.03
3S #1	0.03	3S #2	0.03
4N #1	0.03	4N #2	0.04
4S #1	0.09	4S #2	0.07
5N #1	0.36	5N #2	0.33
5S #1	0.10	5S #2	0.12
6N #1	0.04	6N #2	0.04
6S #1	<0.02	6S #2	<0.02
7N #1	0.12	7N #2	0.08
7S #1	0.02	7S #2	<0.02
8N #1	0.05	8N #2	0.06
8S #1	0.07	8S #2	0.05
SA #1 *	1.66	SA #2 *	1.46
SB #1 **	0.22	SB #2 **	0.24

* NLB spiked sample: Nominal amount = 1.50 ug/sample
** NLB spiked sample: Nominal amount = 0.20 ug/sample

TABLE 2
RECOVERY AND STORAGE DATA FOR METHYL PARATHION

CONCENTRATION, UG	RECOVERY, UG *	RECOVERY AFTER 14 DAYS, UG
0.20	0.22 ± 0.031	0.20 ± 0.028
0.60	0.57 ± 0.047	0.61 ± 0.066
1.00	1.03 ± 0.088	0.97 ± 0.106

* All recoveries are calculated from duplicate analyses of three spiked tubes at each concentration.

TABLE 3
SAMPLING EFFICIENCY AND CONVERSION STUDY FOR METHYL PARATHION

CONCENTRATION, UG	RECOVERY, UG *
0.20	0.18 ± 0.028
1.00	1.05 ± 0.120

* All recoveries are based on duplicate analyses of three spiked tubes at each concentration. One tube per each concentration was sampled at the NLB laboratory site for 24 hrs at a flow rate of 2 liters/min, then analyzed.

Appendix C

Laboratory Method ADDL003

METHOD ADDL003

METHOD FOR THE DETERMINATION OF
SELECTED ORGANOPHOSPHATE PESTICIDES IN AMBIENT AIR

1. Scope

This document describes a method for the sampling and analysis of parathion, methyl parathion, paroxon, malathion, and diazinon at concentrations normally found in ambient air. The method was developed based on NIOSH, EPA and the California Department of Food and Agriculture published methods.

2. Summary of Method

After sampling using a low-volume system comprising pump, controller, glass fiber pre-filter, and purified XAD-2 absorbant trap, the exposed filter and absorbant are desorbed with 2.0 milliliters of 80/20 isoctane/acetone mixture. Two microliters of the extract are injected using splitless mode technique into a gas chromatographic system equipped with a 30 meter DB-5 capillary column, thermionic detector (TSD), and data system. The resultant peaks are identified by characteristic retention times and quantitated in reference to external standards. The identity of a component may be confirmed by use of a column with different characteristics, a second detector system, or by GC/MS.

3. Interferences/Limitations

3.1 Components having similar GC retention times will interfere, causing misidentification and/or erroneous quantitation.

3.2 Extreme care must be taken to insure that sample losses do not occur due to leaks in the sampling system or to sample handling within the laboratory. All glassware must be thoroughly cleaned to insure that cross-contamination does not occur between samples. Samples are to be protected from sunlight during sampling and storage.

4. Apparatus

4.1 Varian Model 3300 Gas Chromatograph equipped with thermionic detector (TSD) and a Vista 402 Data System.

4.2 DB-5 fused silica capillary column, 30 meters x 0.35 mm i.d., 1 um film thickness.

4.3 Amber vials, 3.7 ml capacity, with teflon-lined septum caps.

4.4 Sample agitator with timer and sample rack.

4.5 Microliter syringes, 5-50 µl sizes.

4.6 Low-volume sampler pump and flow controller capable of maintaining preset flow rates of 6 lpm over a 24 hour period. Sampling system must have an accurate timer system to control sampling interval and to indicate total sampling elapsed time.

4.7 Sampling head capable of containing a 37 mm glass fiber filter in-line with a 6" x 1/4" absorption tube containing XAD-2 absorbant.

4.8 Glass fiber filters, 37 mm diameter, type A/E, with teflon holder.

4.9 Glass absorption tubes, 6" x 1/4", containing purified XAD-2 absorbant; 400 mg primary section, 200 mg secondary section. Absorbant must be demonstrated to be free of interfering substances by analysis of unused absorbants (analytical blanks).

5. Reagents

5.1 80/20 iso-octane/acetone desorbant solvent: Mix 80 ml pesticide grade iso-octane (trimethyl pentane) and 20 ml pesticide grade acetone in a clean glass bottle equipped with teflon-lined screw cap. CAUTION: Flammable - DO NOT expose to heat or oxidizers.

5.2 Stock Standards: Individual 1000 µg/ml certified stock standards containing diazion, parathion, methyl parathion, malathion, and paraoxon may be obtained from Nanogens, Inc. CAUTION: Toxic - Use protective gloves in handling these materials.

5.3 Working Standards: Dilute 20 µl of each stock standard into 50/50 isoctane/acetone solvent and dilute to 10.0 ml. This corresponds to 2.0 µg/ml standard.

6. Instrument Conditions

Column: 30 m x ~~0.37~~ 0.32 mm i.d. DB-5 fused silica capillary column

Temperature - Injector: 250°C
Detector: 300°C
Oven: 50°C, initial, hold for 1 minute, ramp at 50°C/min to 140°C/min; ramp at 4°C/min to 260°C, 4 min hold

Flow Rates: Carrier - He, 50 cc/min at splitter, 0.5 min splitless hold, carrier velocity after splitter opens: 25 cm/sec

Detector: TSD - Range 11, Attenuation x 32
Hydrogen Flow: 4.5 cc/min
Air Flow: 180 cc/min
Heater: 3.4 amp

7. Sample Collection

7.1 Sampling flow controllers and indicators must be calibrated by trained personnel before the unit can be installed in the field. The flow rate calibration must be verified monthly at the flow rate used for sampling.

7.2 The 37 mm glass fiber filter and holder, as received from the laboratory, is placed in the sampling head compartment. The compartment is then assembled, taking care that the unit is completely sealed. The filter holder may be handled, but care must be taken not to touch or contaminate the filter itself. If any question of contamination is present, the filter is discarded and a new filter is installed.

7.3 The sealed XAD-2 absorbant tube is prepared for use by snapping off the sealed ends with the tool provided. The open tube is then placed in the sampling train using 1/4" polyethylene tubing fittings, making sure that the flow indicator arrow printed on the tube points in the direction of the flow. The tubing fittings must be tightened sufficiently to insure the system is leak-free.

7.4 After starting the pump system, the flow must be adjusted to approximately 6 lpm. The time, indicated flow reading, and the true flow (read from the calibration graph) must be recorded. The filter and absorbant trap numbers must be recorded. The elapsed time meter is reset to zero. The system is leak-checked by sealing the sampler inlet and insuring that the flow is zero.

7.5 After a 24 hour sampling period, the indicated flow and true flow rates must be recorded. The sampler system is deactivated, the elapsed time and actual time is recorded, and the filter and absorbant tube removed. The filter and cassette holder is placed into a plastic shipping container. The tube is sealed using the red end caps provided. The filter and tube are immediately sent to the laboratory with all sampling information and chain of custody.

8. Instrument Calibration Procedure

8.1 Before a standard solution may be injected, a system blank must be analyzed. This is done by injecting 2.0 µl of 80/20 iso-octane/ acetone solvent for analysis. If the subsequent analysis indicates interferences or contamination, the solvent must be replaced.

8.2 A method blank must be analyzed for every 10 samples. This is done by randomly selecting a "blank" (unused) filter and absorbant tube, desorbing (extracting) the "blank" filter and absorbant, and injecting 2.0 µl of the resultant extract into the instrument for analysis. If interferences or contamination is noted, the source must be found and, if possible, eliminated.

8.3 Instrument calibration is performed by injection of 2.0 µl of 2.0 µg/ml mixed standard. The resultant chromatogram and calculated concentrations must be inspected to insure proper integration and consistency with previous analyses. The data is then used to calibrate the method. The instrument data system will not accept updated response factors which are not within 10 percent of historic data.

8.4 If the analyses are to be made daily, a weekly analysis of three standards (2.0, 0.4, 0.08 µg/ml) must be made to insure that the method exhibits linear response. In addition, a weekly "spiked" sample of 0.8 micrograms per absorbant tube of individual pesticides must be taken through the entire analytical scheme to insure that the method is in control. The results of these analyses must be entered on the method control charts.

9. Analysis of Samples

9.1 After removal of the glass fiber filter from the teflon filter holder using stainless steel forceps, the filter is carefully rolled and placed in a 3.7 ml vial. The filter must be forced into the bottom of the vial to insure tht the entire filter is in contact with the solvent.

9.2 After removal of the red end-caps from the absorbant tube, the tube is scored using a glass cutter above the location of the retainer spring. Using the tool provided, the tube is then broken and the retainer spring removed. The glass wool plug and the primary (400 mg) section of XAD-2 is placed in a 3.7 ml vial. Similarly, the secondary section (200 mg) of XAD-2 is placed in a second vial. Make sure all vials are properly identified.

9.3 Place 2.0 ml desorbing solvent (80/20) into the vials, cap tightly, and place on vial agitator for 45 minutes.

9.4 After desorption, 2.0 µl of each extract is injected into the chromatographic system for analysis. The data generated from the glass fiber filter extract is recorded as "filterable". The combined results are recorded as "total".

9.5 The results are recorded in micrograms/m^3 and are calculated as follows:

$$\mu g/m^3 = \frac{\mu g/ml \text{ (found)} \times 2 \times 1000}{\text{average flow (lpm)} \times \text{time sampled (minutes)}}$$

10. Method Sensitivity, Precision, and Accuracy

10.1 The method sensitivity, precision, and accuracy are outlined in Table I. The data was generated using standards.

11. Desorption Efficiencies and Sample Stability

11.1 The primary section of the XAD-2 sampling tube was "spiked" with 10 µl of solutions containing known amounts of the five organophosphate pesticides of interest. The tubes were then sealed, placed in a refrigerator for storage, and tested after intervals to test the stability of the materials on the sorbont. Table II presents the results of this study. Note that the samples are stable for over a period of two weeks.

11.2 The primary section of the XAD-2 sampling tube was "spiked" with 10 µl of solutions containing known amounts of the five pesticides of interest. The "spiked" tubes were then placed in the low vlume sampling device and sampled at a flow rate of 7.5 lpm for differing lengths of time. Both the primary and secondary sections of the sampling tubes were desorbed and analyzed. The results are presented in Table III. Note that at the sampling rate of 7.5 lpm, the breakthrough volume of all the pesticides tested is greater than 14 m^3.

Table I

Compound	Conc. 1 µg/ml	S.D.* (percent)	Conc. 2 µg/ml	S.D. (percent)	Conc. 3 µg/ml	S.D. (percent)	MDL µg/ml
Diazinon	2.0	11.6	0.4	14	0.08	7	0.04
Methyl Parathion	2.0	2.3	0.4	8	0.08	7	0.02
Paroxon	2.0	11	0.4	12	0.08	11	0.04
Malathion	2.0	9.6	0.4	10	0.08	8	0.04
Parathion	2.0	8.3	0.4	8	0.08	9	0.02

Compound	Correlation Coefficient	Slope	Intercept (µg/ml)
Diazinon	0.998	0.980	0.031
Methyl Parathion	0.998	0.988	0.016
Paroxon	0.997	0.996	0.026
Malathion	0.997	0.991	0.032
Parathion	0.998	1.003	-0.015

* S.D. = Relative Standard Deviation

Table II

ORGANO-PHOSPHATE PESTICIDE STABILITY STUDY

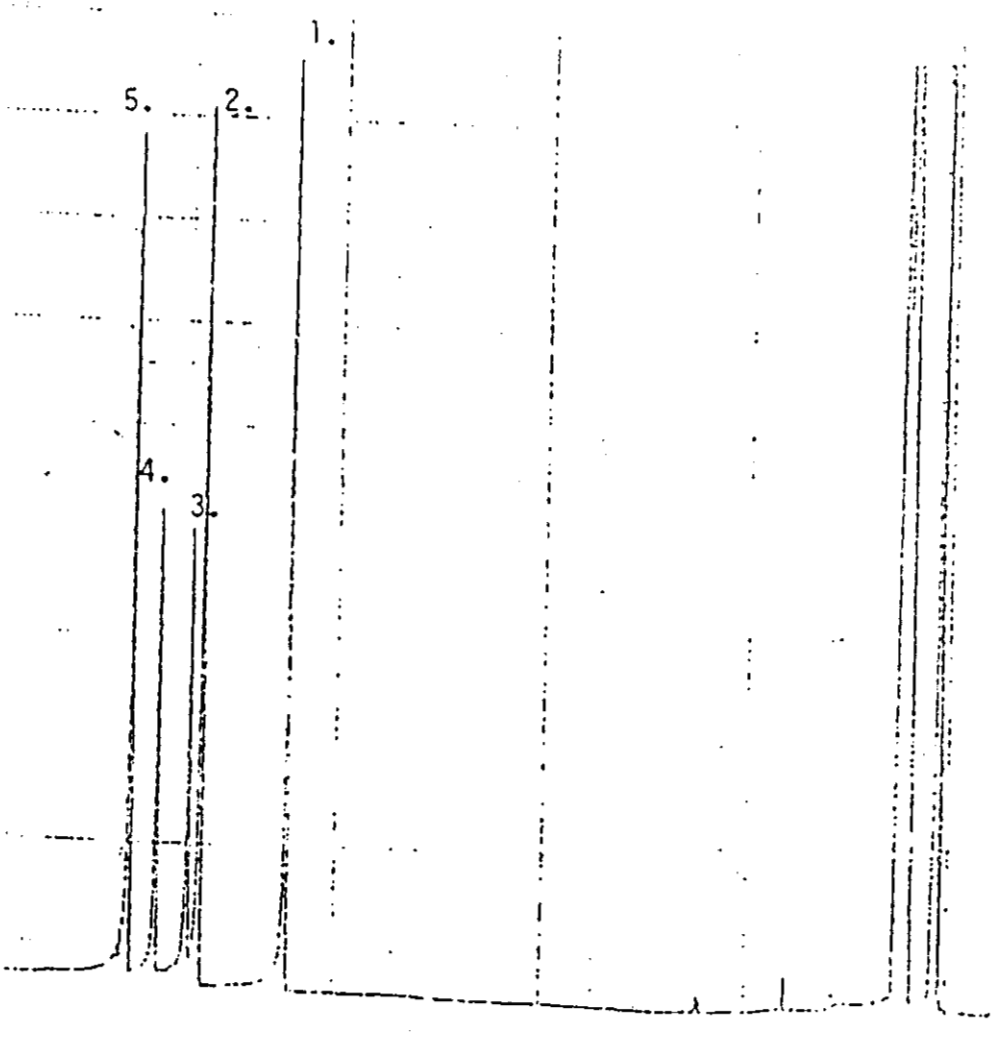
Storage Time, Hrs:	0	24	48	96	192	384
Compound	Amount Recovered, µg (Percent)					
Diazinon	1.68 (98)	1.60 (93)	1.70 (99)	1.58 (92)	1.64 (95)	1.62 (94)
Methyl Parathion	1.45 (83)	1.42 (82)	1.50 (86)	1.40 (80)	1.42 (82)	1.35 (78)
Paroxon	1.42 (97)	1.40 (96)	1.48 (101)	1.38 (94)	1.40 (96)	1.41 (96)
Malathion	1.42 (91)	1.38 (88)	1.50 (96)	1.40 (90)	1.42 (91)	1.48 (95)
Parathion	1,50 (88)	1.52 (89)	1.60 (94)	1.46 (86)	1.50 (88)	1.42 (84)

Table III

ORGANO-PHOSPHATE PESTICIDE SAMPLING AND BREAKTHROUGH STUDY

Volume Sampled (7.5 lpm), m^3	3.6	7.2	10.8	14
Compound	Amount Recovered, µg (percent) Primary/µg (percent) Secondary			
Diazinon	1.60 (93)/0 (0)	1.66 (96)/0 (0)	1.56 (91)/0 (0)	1.92 (100)/0 (0)
Methyl Parathion	1.47 (84)/0 (0)	1.55 (89)/0 (0)	1.44 (83)/0 (0)	1.62 (93)/0 (0)
Paroxon	1.40 (96)/0 (0)	1.48 (101)/0 (0)	1.38 (94)/0 (0)	1.50 (103)/0 (0)
Malathion	1.44 (93)/0 (0)	1.48 (95)/0 (0)	1.40 (90)/0 (0)	1.50 (96)/0 (0)
Parathion	1.52 (89)/0 (0)	1.56 (92)/0 (0)	1.42 (84)/0 (0)	1.56 (92)/0 (0)

CHROMATOGRAPHIC ANALYSIS OF ORGANOPHOSPHATE PESTICIDES



STANDARD: 1.0 ug/ml Mixed Standard
CONDITIONS: DB-5 Capillary Column, 30m, 50°C(1 min.), 50°C/min to 140°C, 4°C/min to 260°C(4 min.); TSD, 3.4 A, Range 11; Helium carrier, 26 cm/sec, splitless.

1. Diazinon
2. Methyl Parathion
3. Paroxon
4. Malathion
5. Parathion